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ON - LINE TEXT VALIDATION

PAGE 1

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E R R O R R E P O R T

PATENT NO: 56571037.001

ISSUE DATE: 09/23/02

GROUP: T1

NO ERRORS FOUND IN THIS PATENT !!

D A C S - E R R O R R E P O R T

PATENT #: 56571037.001

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INFO, NO DACS VALIDATION ERRORS HAVE BEEN FOUND...

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ENDED TEXT DACS VALIDATION FOR: ***** 56571037.001 *****

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--* NEW PATENT *-*-*

Group T1

PATENT # 56571037.001

0001 +pg,1

0002 +sa

0003 A process for producing a silica-based film which
0004 comprises irradiating a film comprising at least one siloxane
0005 compound with electron beams to thereby convert the film into
0006 a film having a dielectric constant of 3 or lower and having
0007 silicon carbide bonds represented by $\text{Si}^{+13}\text{C}^{+13}\text{Si}$ is disclosed.
0008 The film has an even thickness, is excellent in storage
0009 stability, dielectric constant, mechanical strength, etc.,
0010 has low hygroscopicity, and is suitable for use as a dielectric
0011 film in semiconductor devices and the like.
0012 +ea

0013 +pg,2

0014 +su +cl FIELD OF THE INVENTION

0015 +P The present invention relates to a process for
0016 producing a film. More particularly, the invention relates
0017 to a process capable of giving a coating film which is excellent
0018 in dielectric constant, mechanical strength, and low
0019 hygroscopicity, and is suitable for use as a dielectric film
0020 in semiconductor devices and the like.

0021 +cl BACKGROUND OF THE INVENTION

0022 +P Silica (SiO_2) films formed by vacuum processes such as
0023 the CVD method have hitherto been used frequently as dielectric
0024 films in semiconductor devices and other devices. In recent
0025 years, a dielectric film which comprises a tetraalkoxysilane
0026 hydrolyzate as the main component and is called an SOG (spin
0027 on glass) film has come to be used for the purpose of forming
0028 a more even dielectric film. Furthermore, as a result of the
0029 trend toward higher degree of integration in semiconductor
0030 devices and the like, a dielectric film called an organic SOG
0031 film has been developed which comprises a polyorganosiloxane
0032 as the main component and has a low dielectric constant.

0033 +P However, with further progress in the high integration
0034 or multilayer film interconnection in semiconductor devices
0035 and the like, better electrical insulation between metal lines
0036 and vias has come to be required and, hence, a dielectric film
0037 has come to be desired which

0039 +pg,3

0040 characteristics.

0041 +P JP-A-+b 6+1 -+b 181201 +1 (the term +37 JP-A+38 +0 as used herein <<<<
>>>>means

0042 an +37 unexamined published Japanese patent application+38)

0043 discloses a dielectric film having a lower dielectric constant.

0044 This technique is intended to provide an insulating film for

0045 semiconductor devices which has low water absorption and

0046 excellent cracking resistance. This insulating film is formed

0047 from a composition which comprises as the main component an

0048 oligomer having a number average molecular weight of +b 500 +1 or

0049 higher obtained by condensation-polymerizing an

0050 organometallic compound containing at least one element

0051 selected from titanium, zirconium, niobium, and tantalum with

0052 an organosilicon compound having at least one alkoxyl group

0053 in the molecule.

0054 +P JP-A-+b 10+1 -+b 237307 +1 and WO +b 97/00535 +1 disclose <<<<

>>>>techniques for

0055 curing an SOG film with electron beams, which comprise

0056 irradiating a resin comprising a siloxane resin as the main

0057 component with electron beams. These techniques are intended

0058 to convert a siloxane resin into silica (SiO₂+hd 2+1) by electron beam

0059 irradiation. The insulating film thus obtained usually has

0060 a dielectric constant of from +b 3.5 +1 to +b 4.2, +1 which is still too

0061

0063 +CI SUMMARY OF THE INVENTION

0064 +P Accordingly, one object of the invention is to provide

0065

0066 described above. More particularly, the object is to provide

0095 group; $R+hu\ 2\ +1$ represents a monovalent organic group; and a is an

0096 +pg,5

0097 integer of +b 0 +1 to +b 2,

0098 +ps and compounds represented by the following formula (+b 2+1)

0099 (hereinafter referred to as +37 compounds (+b 2+1)+38):

0100 +ps

0101 +ti R+hu 3+hd b+1 (R+hu 4+1 O)+hd 3-b+1 Si+13 (R+hu 7+1)+hd d+1 +13 <<<<
>>>>Si(OR+hu 5+1)+hd 3-c+1 R+hu 6+hd c+tm (+b 2+1)

0102 +ps

0103 +ps wherein R+hu 3+1 , R+hu 4+1 , R+hu 5+1 , and R+hu 6 +1 may be the <<<<
>>>>same or different and each

0104 represents a monovalent organic group; b and c may be the same

0105 or different and each is an integer of +b 0 +1 to +b 2; +1 R+hu 7 +1 <<<<
>>>>represents

0106 an oxygen atom or a group represented by +13 (CH+hd 2+1)+hd n+1 +13 ,<<<<
>>>> wherein n

0107 is +b 1 +1 to +b 6; +1 and d is +b 0 +1 or +b 1.

0108 +P Examples of the monovalent organic groups represented

0109 by R+hu 1 +1 and R+hu 2 +1 in formula (+b 1+1) include alkyl, aryl, <<<<
>>>>allyl, and

0110 glycidyl groups. In formula (+b 1+1), R+hu 1 +1 is preferably a <<<<
>>>>monovalent

0111 organic group, more preferably an alkyl or phenyl group.

0112 +P The alkyl group preferably has +b 1 +1 to +b 5 +1 carbon atoms,

0113 and examples thereof include methyl, ethyl, propyl, and butyl.

0114 These alkyl groups may be

0115 for example, with fluorine atoms.

0117 +P In formula (+b 1+1), examples of the aryl group include

0118 phenyl, tolyl, p-tolyl, m-tolyl, o-tolyl, naphthyl, biphenyl, and triphenyl.

0119 bromophenyl, and fluorophenyl.

0120 +P Specific examples of the compounds represented by

0121 formula (+b 1+1) include:

0122 +p0 trialkoxysilanes such as trimethoxysilane, triethoxysilane,

0123 tri-n-propoxysilane, triisopropoxysilane, tri-n-butoxysilane,

0124 tri-sec-butoxysilane, tri-tert-butoxysilane,

0125 triphenoxysilane, fluorotrimethoxysilane,

0154 +pg, 7

0155 isopropyltriisopropoxysilane, isopropyltri-n-butoxysilane,

0156 isopropyltri-sec-butoxysilane, isopropyltri-tert-butoxysilane,

0157 isopropyltriphenoxysilane, n-butyltrimethoxysilane,

0158 n-butyltriethoxysilane, n-butyltri-n-propoxysilane,

0159 n-butyltriisopropoxysilane, n-butyltri-n-butoxysilane,

0160 n-butyltri-sec-butoxysilane, n-butyltri-tert-butoxysilane,

0161 n-butyltriphenoxysilane, sec-butyltrimethoxysilane,

0162 sec-butyltriethoxysilane, sec-butyltri-n-propoxysilane,

0163 sec-butyltriisopropoxysilane,

0164 sec-butyltri-n-butoxysilane, sec-butyltri-sec-butoxysilane,

0165 sec-butyltri-tert-butoxysilane, sec-butyltriphenoxysilane,

0166 tert-butyltrimethoxysilane, tert-butyltriethoxysilane,

0167 tert-butyltri-n-propoxysilane, tert-butyltriisopropoxysilane,

0168 tert-butyltri-n-butoxysilane,

0169 tert-butyltri-sec-butoxysilane, and tert-butyltri-tert-butoxysilane;

0170 +p0 tert-butyltriphenoxysilane, phenyltrimethoxysilane,

0171 phenyltriethoxysilane, phenyltri-n-propoxysilane,

0172 phenyltriisopropoxysilane, phenyltri-n-butoxysilane,

0173 phenyltri-sec-butoxysilane, phenyltri-tert-butoxysilane,

0174 phenyltriphenoxysilane, vinyltrimethoxysilane,

0175 vinyltriethoxysilane, +65 -aminopropyltrimethoxysilane, +65

0176 -aminopropyltriethoxysilane, +65

0177 -glycidoxypropyltrimethoxysilane, +65

0178 -glycidoxypropyltriethoxysilane, +65

0179 -glycidoxypropyltriphenoxysilane, +65

0180 -aminopropyltriethoxysilane; and

0181 +pg, 8
0182 +p0 dimethyldimethoxysilane, dimethyldiethoxysilane,
0183 dimethyldi-n-propoxysilane, dimethyldiisopropoxysilane,
0184 dimethyldi-n-butoxysilane, dimethyldi-sec-butoxysilane,
0185 dimethyldi-tert-butoxysilane, dimethyldiphenoxysilane,
0186 diethyldimethoxysilane, diethyldiethoxysilane, diethyldi-n-propoxysilane,
0187 diethyldiisopropoxysilane, diethyldi-n-butoxysilane,
0188 diethyldi-sec-butoxysilane, diethyldi-tert-butoxysilane,
0189 diethyldiphenoxysilane, di-n-propyldimethoxysilane,
0190 di-n-propyldiethoxysilane, di-n-propyldi-n-propoxysilane,
0191 di-n-propyldiisopropoxysilane,
0192 di-n-propyldi-n-butoxysilane, di-n-propyldi-sec-butoxysilane,
0193 di-n-propyldi-tert-butoxysilane, di-n-propyldiphenoxysilane,
0194 diisopropyldimethoxysilane,
0195 diisopropyldiethoxysilane, diisopropyldi-n-propoxysilane,
0196 diisopropyldiisopropoxysilane, diisopropyldi-n-butoxysilane,
0197 diisopropyldi-sec-butoxysilane, diisopropyldi-tert-butoxysilane,
0198 diisopropyldiphenoxysilane, di-n-butyldimethoxysilane,
0199 di-n-butyldiethoxysilane, di-n-butyldi-n-propoxysilane,
0200 di-n-butyldiisopropoxysilane, di-n-butyldi-n-butoxysilane,
0201 di-n-butyldi-sec-butoxysilane,
0202 di-n-butyldi-tert-butoxysilane, di-n-butyldiphenoxysilane,
0203 di-sec-butyldimethoxysilane, di-sec-butyldiethoxysilane,
0204 di-sec-butyldi-n-propoxysilane, di-sec-butyldiisopropoxysilane,
0205 di-sec-butyldiphenoxysilane,
0206 di-tert-butyldimethoxysilane,
0207 di-sec-butyldiphenoxysilane, di-tert-butyldimethoxysilane,
0208 di-tert-butyldiethoxysilane, di-tert-butyldi-n-propoxysilane,

- 0209 +pg, 9
- 0210 di-tert-butyldiisopropoxysilane,
- 0211 di-tert-butyldi-n-butoxysilane,
- 0212 di-tert-butyldi-sec-butoxysilane, di-tert-butyldi-tert-butoxysilane,
- 0213 di-tert-butyldiphenoxysilane,
- 0214 diphenyldimethoxysilane, diphenyldiethoxysilane,
- 0215 diphenyldi-n-propoxysilane, diphenyldiisopropoxysilane,
- 0216 diphenyldi-n-butoxysilane, diphenyldi-sec-butoxysilane,
- 0217 diphenyldi-tert-butoxysilane, diphenyldiphenoxysilane,
- 0218 divinyltrimethoxysilane, +65 -aminopropyltrimethoxysilane, +65
- 0219 -aminopropyltriethoxysilane, +65
- 0220 -glycidoxypropyltrimethoxysilane, +65
- 0221 -glycidoxypropyltriethoxysilane, +65
- 0222 -trifluoropropyltrimethoxysilane, and +65
- 0223 -trifluoropropyltriethoxysilane.
- 0224 +P Preferred of those compounds (+b 1+1) are
- 0225 tetramethoxysilane, tetraethoxysilane, tetra-n-propoxysilane,
- 0226 tetraisopropoxysilane, tetraphenoxysilane,
- 0227 methyltrimethoxysilane, methyltriethoxysilane, methyltri-n-propoxysilane,
- 0228 methyltriisopropoxysilane,
- 0229 ethyltrimethoxysilane, ethyltriethoxysilane,
- 0230 vinyltrimethoxysilane, vinyltriethoxysilane,
- 0231 phenyltrimethoxysilane, phenyltriethoxysilane,
- 0232 dimethyldimethoxysilane, dimethyldiethoxysilane,
- 0233 diethyldimethoxysilane, diethyldiethoxysilane,
- 0234 trimethylmonomethoxysilane, trimethylmonoethoxysilane,
- 0235 triethylmonomethoxysilane, triethylmonoethoxysilane,
- 0236 triethylmonomethoxysilane, triethylmonoethoxysilane,

0237 +pg, 10

0238 triphenylmonomethoxysilane, and triphenylmonoethoxysilane.

0239 +P In formula (+b 2+1), examples of the monovalent organic

0240 group include the same organic groups as those enumerated above

0241 with regard to formula (+b 1+1).

0242 +P Examples of the divalent organic group represented by

0243 R+hu 7 +1 in formula (+b 2+1) include alkylene groups having +b 2 +1 <<<<
>>>>to +b 6 +1 carbon

0244 atoms, such as methylene.

0245 +P Examples of the compounds represented by formula (+b 2+1)

0246 wherein R^{hu 7 +1} is an oxygen atom include hexamethoxydisiloxane,

0247 hexaethoxydisiloxane, hexaphenoxydisiloxane, +b 1,1,1,3,3+1

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0248  -pentamethoxy-+b 3+1 -methylidisiloxane, +b 1,1,1,3,3+1 -pentaethoxy-<<<<
>>>>+b 3+1
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0249 -methyldisiloxane, +b 1,1,1,3,3+1 -pentamethoxy-+b 3+1 -phenyldisiloxane,

0250 +b 1,1,1,3,3+1 -pentaethoxy-+b 3+1 -phenyldisiloxane, +b 1,1,3,3+1

0251 -tetramethoxy-+b 1,3+1 -dimethyldisiloxane, +b 1,1,3,3+1 -tetraethoxy-+b

0252 1,3+1 -dimethyldisiloxane, +b 1,1,3,3+1 -tetramethoxy-+b 1,3+1

0253 -diphenyldisiloxane, +b 1,1,3,3+1 -tetraethoxy-+b 1,3+1

0254 -diphenyldisiloxane, +b 1,1,3,+l -trimethoxy-+b 1,3,3+l

0255 -trimethyldisiloxane, +b 1,1,3+1 -triethoxy-+b 1,3,3+1

0256 -trimethyldisiloxane, +b 1,1,3+1 -trimethoxy-+b 1,3,3+1

0257 -triphenyldisiloxane, +b 1,1,3+1 -triethoxy-+b 1,3,3+1

0258 -triphenyldisiloxane, +b 1,3+1 -dimethoxy-+b 1,1,3,3+1

0259 tetramethyldiciloxane 1 1 1 1

204 tetraphenyldisiloxane, and +b 1,3+1 -diethoxy-+b 1,1,3,3+1

0262 -tetraphenyldisiloxane. Preferred of these are

0264 -tetramethoxy-+b 1,3+1 -dimethyldisiloxane, +b 1,1,3,3+1 -tetraethoxy-+b

0265 +pg, 11

0266 1,3+1 -dimethyldisiloxane, +b 1,1,3,3+1 -tetramethoxy-+b 1,3+1

0267 -diphenyldisiloxane, +b 1,3+1 -dimethoxy-+b 1,1,3,3+1

0268 -tetramethyldisiloxane, +b 1,3+1 -diethoxy-+b 1,1,3,3+1

0269 -tetramethyldisiloxane, +b 1,3+1 -dimethoxy-+b 1,1,3,3+1

0270 -tetraphenyldisiloxane, +b 1,3+1 -diethoxy-+b 1,1,3,3+1

0271 -tetraphenyldisiloxane, and the like.

0272 +P Examples of the compounds represented by formula (+b 2+1)

0273 wherein d is +b 0 +1 include hexamethoxydisilane.

0274 hexaethoxydisilane, hexaphenoxydisilane, +b 1,1,1,2,2+1

0275 -pentamethoxy-+b 2+1 -methyldisilane, +b 1,1,1,2,2+1 -pentaethoxy-+b 2+1

0276 -methyldisilane, +b 1,1,1,2,2+1 -pentamethoxy-+b 2+1 -phenyldisilane,

0277 +b 1,1,1,2,2+1 -pentaethoxy-+b 2+1 -phenyldisilane, +b 1,1,2,2+1

0278 -tetramethoxy-+b 1,2+1 -dimethyldisilane, +b 1,1,2,2+1 -tetraethoxy-+b

0279 1,2+1 -dimethyldisilane, +b 1,1,2,2+1 -tetramethoxy-+b 1,2+1

0280 -diphenyldisilane, +b 1,1,2,2+1 -tetraethoxy-+b 1,2+1 -diphenyldisilane,

0281 +b 1,1,2+1 -trimethoxy-+b 1,2,2+1 -trimethyldisilane, +b 1,1,2+1 -<<<<

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>>>>triethoxy-+b
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0282 1,2,2+1 -trimethyldisilane, +b 1,1,2+1 -trimethoxy-+b 1,2,2+1

0283 -triphenyldisilane, +b 1,1,2+1 -triethoxy-+b 1,2,2+1 -triphenyldisilane,

0284 +b 1,2+1 -dimethoxy-+b 1,1,2,2+1 -tetramethyldisilane, +b 1,2+1 -<<<<

>>>>diethoxy-+b

0285 1,1,2,2+1 -tetramethyldisilane, +b 1,2+1 -dimethoxy-+b 1,1,2,2+1

0286 -tetraphenyldisilane, and +b 1,2+1 -diethoxy-+b 1,1,2,2+1

0287 - tetraphenyl disilane

wherein $K+n+1$ is a group represented by $+13 (CH+hd^{2+1})+hd^{n+1} <<<<$

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>>>>+13 +0 include
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0291 bis(hexaphenoxysilyl)methane,

0292 bis(dimethoxymethylsilyl)methane,

- 0293 +pg,12
- 0294 bis(diethoxymethylsilyl)methane,
- 0295 bis(dimethoxyphenylsilyl)methane,
- 0296 bis(diethoxyphenylsilyl)methane,
- 0297 bis(methoxydimethylsilyl)methane,
- 0298 bis(ethoxydimethylsilyl)methane,
- 0299 bis(methoxydiphenylsilyl)methane,
- 0300 bis(ethoxydiphenylsilyl)methane,
- 0301 bis(hexamethoxysilyl)ethane, bis(hexaethoxysilyl)ethane,
- 0302 bis(hexaphenoxysilyl)ethane,
- 0303 bis(dimethoxymethylsilyl) ethane,
- 0304 bis(diethoxymethylsilyl)ethane,
- 0305 bis(dimethoxyphenylsilyl)ethane,
- 0306 bis(diethoxyphenylsilyl)ethane,
- 0307 bis(methoxydimethylsilyl)ethane,
- 0308 bis(ethoxydimethylsilyl)ethane,
- 0309 bis(methoxydiphenylsilyl)ethane,
- 0310 bis(ethoxydiphenylsilyl)ethane, +b 1,3+1
- 0311 -bis(hexamethoxysilyl)propane, +b 1,3+1
- 0312 -bis(hexaethoxysilyl)propane, +b 1,3+1
- 0313 -bis(hexaphenoxysilyl)propane, +b 1,3+1
- 0314 -bis(dimethoxymethylsilyl)propane, +b 1,3+1
- 0315 -bis(diethoxymethylsilyl)propane, +b 1,3+1
- 0316 -bis(dimethoxyphenylsilyl)propane, +b 1,3+1
- 0319 -bis(ethoxydimethylsilyl)propane, +b 1,3+1
- 0320 -bis(methoxydiphenylsilyl)propane, and +b 1,3+1

0347 is generally from +b 25 +1 to +b 95+1 % by weight, preferably from +b <<<<
>>>>30 +1 to

0348 +b 90+1 % by weight, more preferably from +b 30 +1 to +b 85+1 % by <<<<
>>>>weight, in

0349 +pg,14

0350 terms of the amount of the product of complete hydrolysis and
 0351 condensation. When a tetraalkoxysilane and a trialkoxysilane
 0352 are used in a proportion within that range, the coating film
 0353 obtained has a high modulus of elasticity and an exceedingly
 0354 low dielectric constant.

0355 +P The term +37 product of complete hydrolysis and
 0356 condensation+38 +0 as used herein means a product in which all the
 0357 $R+hu\ 2+1\ O+13$, $R+hu\ 4+1\ O+13$, and $R+hu\ 5+1\ O+13\ +0$ groups in the <<<<
 >>>>compounds (+b 1+1) and (+b 2+1) have

0358 been hydrolyzed into SiOH groups and completely condensed to
 0359 form a siloxane structure.

0360 +P The compounds (+b 1+1) and (+b 2+1) are hydrolyzed and condensed
 0361 in an organic solvent. Water is preferably used in the
 0362 hydrolysis and condensation in an amount of from +b 0.3 +1 to +b 10 <<<<
 >>>>+1 mol

0363 per mol of the groups represented by $R+hu\ 2+1\ O+13$, $R+hu\ 4+1\ O+13$, <<<<
 >>>>and $R+hu\ 5+1\ O+13\ +0$ in

0364 formulae (+b 1+1) and (+b 2+1) .

0365 +P A catalyst is generally used for the hydrolysis and
 0366 condensation of the compounds (+b 1+1) and (+b 2+1) in an organic <<<<
 >>>>solvent.

0367 +P Examples of the catalyst include organic acids,
 0368 inorganic acids, organic bases, inorganic bases, and metal
 0369 chelates

0370 propionic acid, butanoic acid, pentanoic acid, hexanoic acid,
 0371 heptanoic acid, octanoic acid, nonanoic acid, decanoic acid,
 0372

0373

0374 sebacic acid, gallic acid, butyric acid, mellitic acid,
0375 arachidonic acid, shikimic acid, +b 2+1 -ethylhexanoic acid, oleic
0376 acid, stearic acid, linoleic acid, linolenic acid, salicylic

0377 +pg,15

0378 acid, benzoic acid, p-aminobenzoic acid, p-toluenesulfonic

0379 acid, benzenesulfonic acid, monochloroacetic acid,

0380 dichloroacetic acid, trichloroacetic acid, trifluoroacetic

0381 acid, formic acid, malonic acid, sulfonic acids, phthalic acid,

0382 fumaric acid, citric acid, and tartaric acid.

0383 +P Examples of the inorganic acids include hydrochloric

0384 acid, nitric acid, sulfuric acid, hydrofluoric acid, and

0385 phosphoric acid.

0386 +P Examples of the inorganic bases include ammonia,

0387 sodium hydroxide, potassium hydroxide, barium hydroxide, and

0388 calcium hydroxide.

0389 +P Examples of the organic bases include methanolamine,

0390 ethanolamine, propanolamine, butanolamine, N-methylmethanolamine,

0391 N-ethylmethanolamine, N-propylmethanolamine,

0392 N-butylmethanolamine, N-methylethanolamine,

0393 N-ethylethanolamine, N-propylethanolamine,

0394 N-butylethanolamine, N-methylpropanolamine,

0395 N-ethylpropanolamine, N-propylpropanolamine,

0396 N-butylpropanolamine, N-methylbutanolamine,

0397 N-ethylbutanolamine, N-propylbutanolamine,

0398 N-butylbutanolamine, N,N-dimethylmethanolamine,

0399 N,N-diethylmethanolamine, N,N-dipropylmethanolamine,

0400 N,N-dibutylmethanolamine, N,N-dimethylethanolamine,

0401 N,N-diethylethanolamine, N,N-dipropylethanolamine,

0402 N,N-dibutylethanolamine, N,N-dimethylpropanolamine,

0403 N,N-diethylpropanolamine, N,N-dipropylpropanolamine,

0404 N,N-dibutylpropanolamine, N,N-dimethylbutanolamine,

0405 +pg,16

- 0406 N,N-diethylbutanolamine, N,N-dipropylbutanolamine,
- 0407 N,N-dibutylbutanolamine, N-methyldimethanolamine,
- 0408 N-ethyldimethanolamine, N-propyldimethanolamine,
- 0409 N-butyldimethanolamine, N-methyldiethanolamine,
- 0410 N-ethyldiethanolamine, N-propyldiethanolamine,
- 0411 N-butyldiethanolamine, N-methyldipropanolamine,
- 0412 N-ethyldipropanolamine, N-propyldipropanolamine,
- 0413 N-butyldipropanolamine, N-methyldibutanolamine,
- 0414 N-ethyldibutanolamine, N-propyldibutanolamine,
- 0415 N-butyldibutanolamine, N-(aminomethyl)methanolamine,
- 0416 N-(aminomethyl)ethanolamine,
- 0417 N-(aminomethyl)propanolamine, N-(aminomethyl)butanolamine,
- 0418 N-(aminoethyl)methanolamine, N-(aminoethyl)ethanolamine,
- 0419 N-(aminoethyl)propanolamine, N-(aminoethyl)butanolamine,
- 0420 N-(aminopropyl)methanolamine, N-(aminopropyl)ethanolamine,
- 0421 N-(aminopropyl)propanolamine, N-(aminopropyl)butanolamine,
- 0422 N-(aminobutyl)methanolamine, N-(aminobutyl)ethanolamine,
- 0423 N-(aminobutyl)propanolamine, N-(aminobutyl)butanolamine,
- 0424 methoxymethylamine, methoxyethylamine, methoxypropylamine,
- 0425 methoxybutylamine, ethoxymethylamine, ethoxyethylamine,
- 0426 ethoxypropylamine, ethoxybutylamine, propoxymethylamine,
- 0427 propoxyethylamine, propoxypropylamine, propoxybutylamine,
- 0428 butoxymethylamine, butoxyethylamine, butoxypropylamine,
- 0429
- 0430
- 0431 N,N-dibutylamine, trimethylamine,
- 0432 triethylamine, tripropylamine, tributylamine,

0433 +pg,17

0434 tetramethylammonium hydroxide, tetraethylammonium hydroxide,

0435 tetrapropylammonium hydroxide, tetrabutylammonium hydroxide,

0436 tetramethylethylenediamine, tetraethylethylenediamine,

0437 tetrapropylethylenediamine, tetrabutylethylenediamine,

0438 methylaminomethylamine, methylaminoethylamine,

0439 methylaminopropylamine, methylaminobutylamine,

0440 ethylaminomethylamine, ethylaminoethylamine,

0441 ethylaminopropylamine, ethylaminobutylamine,

0442 propylaminomethylamine, propylaminoethylamine,

0443 propylaminopropylamine, propylaminobutylamine,

0444 butylaminomethylamine, butylaminoethylamine,

0445 butylaminopropylamine, butylaminobutylamine, pyridine,

0446 pyrrole, piperazine, pyrrolidine, piperidine, picoline,

0447 morpholine, methylmorpholine, diazabicyclooctane,

0448 diazabicyclononane, diazabicycloundecene, and urea.

0449 +P Examples of the metal chelates include titanium

0450 chelate compounds such as

0451 triethoxymono(acetylacetonato)titanium, tri-n-propoxymono(acetylaceto<<<<
>>>>nato)titanium,

0452 triisopropoxymono(acetylacetonato)titanium, tri-n-butoxymono(acetylac<<<<
>>>>etonato)titanium,

0453 tri-sec-butoxymono(acetylacetonato)titanium,

0454 tri-tert-butoxymono(acetylacetonato)titanium,

0455 tri-n-butoxybis(acetylacetonato)titanium,

0456 diisopropoxybis(acetylacetonato)titanium, di-n-butoxybis(acetylaceton<<<<
>>>>ato)titanium,

0457 di-tert-butoxybis(acetylacetonato)titanium,

0458 +pg, 18

0459 di-tert-butoxybis(acetylacetonato)titanium,

0460 monoethoxytris(acetylacetonato)titanium, mono-n-propoxytris(acetylacetonato)titanium,

0461 monoisopropoxytris(acetylacetonato)titanium, mono-n-butoxytris(acetylacetonato)titanium,

0462 mono-sec-butoxytris(acetylacetonato)titanium,

0463 mono-tert-butoxytris(acetylacetonato)titanium,

0464 tetrakis(acetylacetonato)titanium,

0465 triethoxymono(ethylacetoacetato)titanium, tri-n-propoxymono(ethylacetoacetato)titanium,

0466 triisopropoxymono(ethylacetoacetato)titanium, tri-n-butoxymono(ethylacetoacetato)titanium,

0467 tri-sec-butoxymono(ethylacetoacetato)titanium,

0468 tri-tert-butoxymono(ethylacetoacetato)titanium,

0469 diethoxybis(ethylacetoacetato)titanium, di-n-propoxybis(ethylacetoacetato)titanium,

0470 disopropoxybis(ethylacetoacetato)titanium, di-n-butoxybis(ethylacetoacetato)titanium,

0471 di-sec-butoxybis(ethylacetoacetato)titanium, di-tert-butoxybis(ethylacetoacetato)titanium,

0472 monoethoxytris(ethylacetoacetato)titanium, mono-n-propoxytris(ethylacetoacetato)titanium,

0473 monoisopropoxytris(ethylacetoacetato)titanium, mono-n-butoxytris(ethylacetoacetato)titanium,

0474 mono-tert-butoxytris(ethylacetoacetato)titanium,

0476 +pg,19

0477 tetrakis(ethylacetoacetato)titanium,

0478 mono(acetylacetonato)tris(ethylacetoacetato)titanium,

0479 bis(acetylacetonato)bis(ethylacetoacetato)titanium, and

0480 tris(acetylacetonato)mono(ethylacetoacetato)titanium;

0481 zirconium chelate compounds such as

0482 triethoxymono(acetylacetonato)zirconium, tri-n-propoxymono(acetylacet<<<<
>>>>onato)zirconium,

0483 triisopropoxymono(acetylacetonato)zirconium, tri-n-butoxymono(acetyla<<<<
>>>>cetonato)zirconium,

0484 tri-sec-butoxymono(acetylacetonato)zirconium,

0485 tri-tert-butoxymono(acetylacetonato)zirconium,

0486 diethoxybis(acetylacetonato)zirconium, di-n-propoxybis(acetylacetonat<<<<
>>>>o)zirconium,

0487 disopropoxybis(acetylacetonato)zirconium, di-n-butoxybis(acetylaceton<<<<
>>>>ato)zirconium,

0488 di-sec-butoxybis(acetylacetonato)zirconium,

0489 di-tert-butoxybis(acetylacetonato)zirconium,

0490 monoethoxytris(acetylacetonato)zirconium, mono-n-propoxytris(acetylac<<<<
>>>>etonato)zirconium,

0491 monoisopropoxytris (acetylacetonato) zirconium, mono-n-butoxytris(ace<<<<
>>>>tylacetonato)zirconium,

0492 mono-sec-butoxytris(acetylacetonato)zirconium,

0493 mono-tert-butoxytris(acetylacetonato)zirconium,

>>>>toacetato)zirconium,

0496 triisopropoxymono(ethylacetoacetato)zirconium, tri-n-butoxymono(ethyl<<<<

0497 +pg, 20

0498 tri-sec-butoxymono(ethylacetoacetato)zirconium,

0499 tri-tert-butoxymono(ethylacetoacetato)zirconium,

0500 diethoxybis(ethylacetoacetato)zirconium, di-n-propoxybis(ethylacetoac<<<<
>>>>etato)zirconium,

0501 diisopropoxybis(ethylacetoacetato)zirconium, di-n-butoxybis(ethylacet<<<<
>>>>oacetato)zirconium,

0502 di-sec-butoxybis(ethylacetoacetato)zirconium,

0503 di-tert-butoxybis(ethylacetoacetato)zirconium,

0504 monoethoxytris(ethylacetoacetato)zirconium, mono-n-propoxytris(ethyla<<<<
>>>>cetoacetato)zirconium,

0505 monoisopropoxytris(ethylacetoacetato)zirconium, mono-n-butoxytris(eth<<<<
>>>>ylacetoacetato)zirconium,

0506 mono-sec-butoxytris(ethylacetoacetato)zirconium,

0507 mono-tert-butoxytris(ethylacetoacetato)zirconium,

0508 tetrakis(ethylacetoacetato)zirconium,

0509 mono(acetylacetonato)tris(ethylacetoacetato)zirconium,

0510 bis(acetylacetonato)bis(ethylacetoacetato)zirconium, and

0511 tris(acetylacetonato)mono(ethylacetoacetato)zirconium; and

0512 aluminum chelate compounds such as

0513 tris(acetylacetonato)aluminum and

0514 tris(ethylacetoacetato)aluminum.

0515 +P The amount of the catalyst to be used is generally from

0516 +b 0.0001 +l to +b 1 +l mol, preferably from +b 0.001 +l to +b 0.1 +l <<<<

0518 +P In the case where the siloxane compound is a condensate,

0519 it preferably has a weight-average molecular weight.

0520 +pg, 21

0521 calculated for standard polystyrene, of from +b 500 +1 to +b 100,000.

0522 +P In the invention, the siloxane compound is usually

0523 dissolved in an organic solvent and applied as a coating

0524 composition.

0525 +P Examples of the solvent which can be used in the

0526 invention include aliphatic hydrocarbon solvents such as

0527 n-pentane, isopentane, n-hexane, isohexane, n-heptane,

0528 isoheptane, +b 2,2,4+1 -trimethylpentane, n-octane, isooctane,

0529 cyclohexane, and methylcyclohexane; aromatic hydrocarbon

0530 solvents such as benzene, toluene, xylene, ethylbenzene,

0531 trimethylbenzene, methylethylbenzene, n-propylbenzene,

0532 isopropylbenzene, diethylbenzene, isobutylbenzene,

0533 triethylbenzene, diisopropylbenzene, n-amylnaphthalene, and

0534 trimethylbenzene; monohydric alcohols such as methanol,

0535 ethanol, n-propanol, isopropanol, n-butanol, isobutanol,

0536 sec-butanol, t-butanol, n-pentanol, isopentanol, +b 2+1

0537 -methylbutanol, sec-pentanol, t-pentanol, +b 3+1 -methoxybutanol,

0538 n-hexanol, +b 2+1 -methylpentanol, sec-hexanol, +b 2+1 -ethylbutanol,

0539 sec-heptanol, heptanol-+b 3, +1 n-octanol, +b 2+1 -ethylhexanol, sec-
>>>>octanol,

0540 n-nonyl alcohol, +b 2,6+1 -dimethylheptanol-+b 4, +1 n-decanol,

0541 sec-undecyl alcohol, trimethylnonyl alcohol, sec-tetradecyl

0542 alcohol, sec-heptadecyl alcohol, phenol, cyclohexanol,

0543 methanol, ethanol, n-propanol, isopropanol, n-butanol, isobutanol,

0544 sec-butanol, t-butanol, n-pentanol, isopentanol, +b 2+1

0545 polyhydric alcohols such as ethylene glycol, +b 1,2+1 -propylene

0546 glycol, +b 1,3+1 -butylene glycol, pentanediol-+b 2,4, 2+1

0547 pentanediol-+b 1,3, 2+1, hexanediol-+b 2,4, 2+1, heptanediol-+b 2,4, 2+1,

>>>>4, 2+1

0548 +pg,22

0549 -ethylhexanediol-+b 1,3, +1 diethylene glycol, dipropylene glycol,
0550 triethylene glycol, tripropylene glycol, and glycerol; ketone
0551 solvents such as acetone, methyl ethyl ketone, methyl n-propyl
0552 ketone, methyl n-butyl ketone, diethyl ketone, methyl isobutyl
0553 ketone, methyl n-pentyl ketone, ethyl n-butyl ketone, methyl
0554 n-hexyl ketone, diisobutyl ketone, trimethylnonanone,
0555 cyclohexanone, methylcyclohexanone, +b 2,4+1 -pentanedione,
0556 acetonylacetone, diacetone alcohol, acetophenone, and
0557 fenchone; ether solvents such as ethyl ether, isopropyl ether,
0558 n-butyl ether, n-hexyl ether, +b 2+1 -ethylhexyl ether, ethylene
0559 oxide, +b 1,2+1 -propylene oxide, dioxolane, +b 4+1 -methyldioxolane,
0560 dioxane, dimethyldioxane, ethylene glycol monomethyl ether,
0561 ethylene glycol monoethyl ether, ethylene glycol diethyl ether,
0562 ethylene glycol mono-n-butyl ether, ethylene glycol mono-n-hexyl
0563 ether, ethylene glycol monophenyl ether, ethylene
0564 glycol mono-+b 2+1 -ethylbutyl ether, ethylene glycol dibutyl ether,
0565 diethylene glycol monomethyl ether, diethylene glycol
0566 monoethyl ether, diethylene glycol diethyl ether, diethylene
0567 glycol mono-n-butyl ether, diethylene glycol di-n-butyl ether,
0568 diethylene glycol mono-n-hexyl ether, ethoxytriglycol,
0569 tetraethylene glycol di-n-butyl ether, propylene glycol
0570 monomethyl ether, propylene glycol monoethyl ether, propylene
0571 glycol monopropyl ether, propylene glycol monobutyl ether,
0572
0573
0574 tetrahydrofuran, and +b 2+1 -methyltetrahydrofuran; ester solvents
0575 such as diethyl carbonate, methyl acetate, ethyl acetate,

0576 +pg,23

0577 +65 -butyrolactone, +65 -valerolactone, n-propyl acetate, isopropyl
 0578 acetate, n-butyl acetate, isobutyl acetate, sec-butyl acetate,
 0579 n-pentyl acetate, sec-pentyl acetate, +b 3+1 -methoxybutyl acetate,
 0580 methylpentyl acetate, +b 2+1 -ethylbutyl acetate, +b 2+1 -ethylhexyl
 0581 acetate, benzyl acetate, cyclohexyl acetate, methylcyclohexyl
 0582 acetate, n-nonyl acetate, methyl acetoacetate, ethyl
 0583 acetoacetate, ethylene glycol monomethyl ether acetate,
 0584 ethylene glycol monoethyl ether acetate, diethylene glycol
 0585 monomethyl ether acetate, diethylene glycol monoethyl ether
 0586 acetate, diethylene glycol mono-n-butyl ether acetate,
 0587 propylene glycol monomethyl ether acetate, propylene glycol
 0588 monoethyl ether acetate, propylene glycol monopropyl ether
 0589 acetate, propylene glycol monobutyl ether acetate, dipropyl
 0590 glycol monomethyl ether acetate, dipropylene glycol monoethyl
 0591 ether acetate, glycol diacetate, methoxytriglycol acetate,
 0592 ethyl propionate, n-butyl propionate, isoamyl propionate,
 0593 diethyl oxalate, di-n-butyl oxalate, methyl lactate, ethyl
 0594 lactate, n-butyl lactate, n-amyl lactate, diethyl malonate,
 0595 dimethyl phthalate, and diethyl phthalate; nitrogen-containing
 0596 solvents such as N-methylformamide, N,N-dimethylformamide,
 0597 N,N-diethylformamide, acetamide, N-methylacetamide,
 0598 N,N-dimethylacetamide, N-methylpropionamide,
 0599 and N-methylpyrrolidone; and sulfur-containing

0602 sulfolane, and +b 1,3+1 -propanesultone. These solvents can be used
 0603 alone or as a mixture of two or more thereof.

0604 +pg,24

0605 +P It is especially preferred in the invention to use an
0606 organic solvent having a boiling point lower than +b 250+1 +20 +0 C.
0607 Examples thereof include alcohols such as methanol, ethanol,
0608 and isopropanol; polyhydric alcohols such as ethylene glycol
0609 and glycerol; glycol ether solvents such as ethylene glycol
0610 monomethyl ether, ethylene glycol monobutyl ether, diethyl
0611 glycol monoethyl ether, diethylene glycol diethyl ether,
0612 propylene glycol monopropoyl ether, and dipropylene glycol
0613 monoethyl ether; glycol acetate/ether solvents such as
0614 ethylene glycol monomethyl ether acetate, diethylene glycol
0615 monobutyl ether acetate, ethylene glycol diacetate, and
0616 propylene glycol methyl ether acetate; amide solvents such as
0617 N,N-dimethylacetamide, N,N-dimethylformamide, and N-methyl-+b
0618 2+1 -pyrrolidone; ketone solvents such as acetone, methyl
0619 ethyl ketone, methyl isobutyl ketone, acetylacetone, and
0620 methyl amyl ketone; and carboxylic ester solvents such as ethyl
0621 lactate, methoxymethyl propionate, and ethoxyethyl propionate.
0622 These solvents may be used alone or in combination of two or
0623 more thereof.

0624 +P The amount of the organic solvent to be used in the
0625 invention is generally from +b 0.3 +1 to +b 25 +1 times (by weight) the
0626 amount of the siloxane compound (in terms of the product of
0627 complete hydrolysis and condensation).

0630 solvent together with other ingredients according to need.

0631 +ps Other Additives

0632 +pg,25

0633 +p The coating composition for use in the invention may
0634 further contain ingredients such as a colloidal silica,
0635 colloidal alumina, and surfactant.

0636 +P The colloidal silica is a dispersion comprising, for
0637 example, any of the aforementioned hydrophilic organic
0638 solvents and high-purity silicic acid anhydride dispersed
0639 therein. It has an average particle diameter of generally from
0640 +b 5 +l to +b 30 +l nm, preferably from +b 10 +l to +b 20 +l nm, and <<<<
>>>>a solid concentration

0641 of generally about from +b 10 +l to +b 40+l % by weight. Examples of the
0642 colloidal silica include the methanol silica sol and
0643 isopropanol silica sol manufactured by Nissan Chemical
0644 Industries, Ltd., and Oscal, manufactured by Catalysts &
0645 Chemicals Industries Co., Ltd.

0646 +P Examples of the colloidal alumina include Alumina Sol
0647 +b 520, 100, +l and +b 200, +l manufactured by Nissan Chemical <<<<
>>>>Industries,

0648 Ltd., and Alumina Clear Sol and Alumina Sol +b 10 +l and +b 132,
0649 +l manufactured by Kawaken Fine Chemicals Co., Ltd.

0650 +P Examples of the surfactant include nonionic
0651 surfactants, anionic surfactants, cationic surfactants, and
0652 amphoteric surfactants, and further include silicone
0653 surfactants, poly(alkylene oxide) surfactants, and

0656 preferably has a total solid concentration of from +b 2 +l to +b 30+l %
0657 by weight. The total solid concentration thereof is suitably

0658

0659 coating composition has a total solid concentration of from

0660 +pg,26

0661 +b 2 +1 to +b 30+1 % by weight, the composition not only gives a coating
0662 film having an appropriate thickness but has better storage
0663 stability.

0664 +P In the coating composition for use in the invention,
0665 the content of alcohols having a boiling point of +b 100+1 +20 +0 C. <<<<
>>>>or lower

0666 is preferably +b 20+1 % by weight or lower, more preferably +b 5+1 % by
0667 weight or lower. There are cases where alcohols having a
0668 boiling point of +b 100+1 +20 +0 C. or lower generate during the <<<<
>>>>hydrolysis

0669 and condensation of the compounds (+b 1+1) and (+b 2+1). It is <<<<
>>>>therefore

0670 preferred to remove such low-boiling alcohols by distillation
0671 or another means so as to result in a content thereof of +b 20+1 %
0672 by weight or lower, preferably +b 5+1 % by weight or lower.

0673 +P Examples of the substrate to which the coating
0674 composition is applied in the invention include silicon wafers,
0675 SiO₂ wafers, and SiN wafers. Usable coating techniques include
0676 spin coating, dip coating, roll coating, and spraying.

0677 +P The coating film obtained in the invention by applying
0678 the coating composition to a substrate and removing the organic
0679 solvent therefrom has a thickness of generally from +b 0.05 +1 to
0680 +b 3 +1 +82 m, preferably from +b 0.1 +1 to +b 2.5 +1 +82 m.

0681 +P In the invention, the coating film is

0682 irradiated with electron beams.

0684 +P The irradiation with electron beams according to the

0685 method of the invention is carried out at an energy of generally 100 keV or more.

0686 +b 50 +l keV, preferably from +b 1 +l to +b 30 +l keV, in an <<<<
>>>>irradiation dose

0687 of generally from +b 1 +l to +b 1,000 +l +82 C/cm+hu 2+l , preferably <<<<
>>>>from +b 10 +l to +b 500

0688 +pg,27

0689 +l +82 C/cm+hu 2+l .

0690 +P Use of an accelerating voltage of from +b 0.1 +l to +b 50 +l keV
 0691 is advantageous in that electron beams can sufficiently
 0692 penetrate into inner parts of the coating film without passing
 0693 through the film and damaging the underlying semiconductor
 0694 device.

0695 +P Furthermore, when the electron beam irradiation is
 0696 conducted in an irradiation dose of from +b 1 +l to +b 1,000 +l +82 <<<<
 >>>>C/cm+hu 2+l ,

0697 the siloxane compound can be reacted throughout the coating
 0698 film while minimizing damage to the coating film.

0699 +P The temperature of the substrate during the electron
 0700 beam irradiation is generally from +b 25 +l to +b 500+l +20 +0 C., <<<<
 >>>>preferably from

0701 +b 25 +l to +b 450+l +20 +0 C.

0702 +P The time required for the coating film to cure with
 0703 electron beams is generally about from +b 1 +l to +b 5 +l minutes, which
 0704 is far shorter than the time of from +b 15 +l minutes to +b 2 +l hours
 0705 required for thermal cure. It can therefore be said that
 0706 electron beam irradiation is suitable for the treatment of
 0707 individual wafers.

0708 +P Before being irradiated with electron beams according
 0709 to the invention, the coating film may be converted to an

0710 +b 100 +l to +b 1000+l +20 +0 C.

0712 heating the substrate at from +b 250 +l to +b 500+l +20 +0 C. and thereby
 0713 heat-curing the siloxane ingredient according to the

0715 +P The method in which the coating film is heat-cured and

0716 +pg,28

0717 then irradiated with electron beams is effective in reducing
0718 the unevenness of film thickness attributable to unevenness
0719 of electron beam irradiation dose.

0720 +P The electron beam irradiation in the invention is
0721 preferably conducted in an atmosphere having an oxygen
0722 concentration of +b 10,000 +l ppm or lower, preferably +b 1,000 +l ppm or
0723 lower.

0724 +P It is possible to conduct the electron beam irradiation
0725 according to the invention in an inert gas atmosphere.
0726 Examples of the inert gas include nitrogen, helium, argon,
0727 krypton, and xenon. Preferred of these are helium, argon and
0728 nitrogen. When the electron beam irradiation is conducted in
0729 an inert gas atmosphere, the film being irradiated is less apt
0730 to be oxidized, so that a silica-based film retaining a low
0731 dielectric constant can be obtained.

0732 +P The electron beam irradiation may be conducted in an
0733 atmosphere having a reduced pressure. The degree of vacuum
0734 is generally +b 133 +l Pa or lower, preferably from +b 0.133 +l to +b <<<<
>>>>26.7

0735 +l Pa.

0736 +P The silica-based film obtained by the invention has
0737 a carbon content (number of carbon atoms) of generally from
0738 +b 5 +l to +b 17+l % by mole, preferably from +b 9 +l to +b 15.5+l % <<<<

0740 content within that range, it can have improved mechanical
0741 strength while retaining a low dielectric constant.

0743 it has silicon carbide bonds ($\text{Si}^{+13} \text{C}^{+13} \text{Si}$) within the film

0744 +pg,29

0745 structure. In an infrared absorption spectrum, the silicon
0746 carbide bonds give a characteristic absorption around +b 890 +l cm+hu <<<<
>>>>+31 1+l .

0747 +P Because of such features, the silica-based film is
0748 excellent in insulating properties, evenness, dielectric
0749 constant characteristics, cracking resistance, and hardness.

0750 +P Consequently, the silica-based film is useful in
0751 applications such as dielectric films for semiconductor
0752 devices such as LSIs, system LSIs, DRAMs, SDRAMs, RDRAMs, and
0753 D-RDRAMs, protective films such as surface coat films for
0754 semiconductor devices, dielectric films for multilayered
0755 printed circuit boards, and protective or insulating films for
0756 liquid-crystal display devices.

0757 +P The invention will be explained below in more detail
0758 by reference to the following Examples.

0759 +P In the following Examples and Production Example, all
0760 +37 parts+38 +0 and +37 percents+38 +0 are by weight unless otherwise
0761 indicated.

0762 +de +cl PRODUCTION EXAMPLE +b 1

0763 +P An aqueous solution prepared by dissolving +b 1.0 +l g of
0764 maleic acid in +b 157.7 +l g of water was added dropwise over +b 1 +l <<<<
>>>>hour

0765 at room temperature to a solution prepared by mixing +b 101.3 +l g

0768 methyltrimethoxysilane (+b 100.0 +l g in terms of the product of
0769 complete hydrolysis and condensation), +b 97.3 +l g of

methyltrimethoxysilane (+b 100.0 +l g in terms of the product of

0771 complete hydrolysis and condensation), +b 559.3 +1 g of propylene

0772 +pg,30

0773 glycol monopropyl ether, and +b 239.7 +l g of methyl n-pentyl ketone.

0774 After completion of the addition, the resultant mixture was

0775 reacted at +b 60+1 +20 +0 C. for +b 2 +l hours and then concentrated <<<<
>>>>under reduced

0776 pressure until the total solution amount reached +b 1,000 +l g. Thus,

0777 an ingredient (A) solution having a solid content of +b 20+1 % was

0778 obtained.

0779 +cl PRODUCTION EXAMPLE +b 2

0780 +P An aqueous solution prepared by dissolving +b 1.2 +l g of

0781 maleic acid in +b 157.7 +l g of water was added dropwise over +b 1 +l <<<<
>>>>hour

0782 at room temperature to a solution prepared by mixing +b 152.0 +l g

0783 of tetramethoxysilane (+b 60.0 +l g in terms of the product of

0784 complete hydrolysis and condensation), +b 284.1 +l g of

0785 methyltrimethoxysilane (+b 140.0 +l g in terms of the product of

0786 complete hydrolysis and condensation), and +b 798.8 +l g of propylene

0787 glycol monomethyl ether. After completion of the addition,

0788 the resultant mixture was reacted at +b 60+1 +20 +0 C. for +b 2 +l <<<<

>>>>hours and then

0789 concentrated under reduced pressure until the total solution

0790 amount reached +b 1,000 +l g. Thus, an ingredient (A) solution

0791 having a solid content of +b 20+1 % was obtained.

0792 +cl PRODUCTION EXAMPLE +b 3

0793 +cl ethanol

0795 were added +b 15 +l g of methyltrimethoxysilane (+b 7.4 +l g in terms of

0796 the product of complete hydrolysis and condensation) and +b 15 +l g of

0797 +1 g of tetraethoxysilane (+b 5.8 +1 g in terms of the product of
0798 complete hydrolysis and condensation). After this mixture was
0799 reacted at +b 60+1 +20 +0 C. for +b 3 +1 hours, +b 200 +1 g of <<<<
>>>>propylene glycol

0800 +pg,31

0801 monopropyl ether was added thereto. The resultant mixture was
0802 concentrated under reduced pressure until the total solution
0803 amount reached +b 140 +l g. Thereafter, +b 10 +l g of a +b 10+l % <<<<
>>>>acetic acid

0804 solution in propylene glycol monopropyl ether was added thereto.
0805 Thus, a composition solution having a solid content of +b 8.3+l %
0806 was obtained.

0807 +cl PRODUCTION EXAMPLE +b 4

0808 +P In +b 290 +l g of propylene glycol monopropyl ether were
0809 dissolved +b 77.04 +l g of methyltrimethoxysilane, +b 24.05 +l g of
0810 tetramethoxysilane, and +b 0.48 +l g of
0811 tetrakis(acetylacetonato)titanium in a separable flask made
0812 of quartz. This solution was stirred with Three-One Motor and
0813 the temperature of the solution was kept at +b 60+l +20 +0 C. Thereto was
0814 added +b 84 +l g of ion-exchanged water over +b 1 +l hour. The resultant
0815 mixture was reacted at +b 60+l +20 +0 C. for +b 2 +l hours and +b 25 <<<<
>>>>+l g of acetylacetone

0816 was then added. This reaction mixture was further reacted for
0817 +b 30 +l minutes and then cooled to room temperature. From the
0818 reaction mixture was removed +b 149 +l g of a solution comprising
0819 methanol and water by evaporation at +b 50+l +20 +0 C. Thus, a reaction
0820 mixture was obtained.

0821 +P The product of condensation and other reaction thus

0824 +P To a solution prepared by mixing +b 6 +l g of +b 40+l % aqueous
0825 methylamine solution, +b 228 +l g of ultrapure water, and +b 570 +l g of
+b 10+l % methyltrimethoxysilane, +b 24.05 +l g of tetramethoxysilane, and +b 0.48 +l g of

0827 terms of the product of complete hydrolysis and condensation)

0828 +pg,32

0829 and +b 20.9 +l g of tetraethoxysilane (+b 6 +l g in terms of the product
0830 of complete hydrolysis and condensation). After this mixture
0831 was reacted at +b 60+1 +20 +0 C. for +b 2 +l hours, +b 200 +l g of <<<<
>>>>propylene glycol

0832 monopropyl ether was added thereto. The resulting mixture was
0833 concentrated under reduced pressure until the total solution
0834 amount reached +b 116 +l g. Thereafter, +b 10 +l g of a +b 10+1 % <<<<
>>>>acetic acid

0835 solution in propylene glycol monopropyl ether was added thereto.
0836 Thus, a coating composition +b 5 +l having a solid content of +b 10+1 %
0837 was obtained.

0838 +cl EXAMPLE +b 1

0839 +P The coating composition +b 1 +l obtained in Production
0840 Example +b 1 +l was applied to an +b 8+1 -inch silicon wafer by spin <<<<
>>>>coating

0841 to obtain a coating film having a thickness of +b 0.7 +l +82 m. This
0842 coating film was heated first at +b 80+1 +20 +0 C. in the air for +b <<<<
>>>>5 +l minutes

0843 and subsequently at +b 200+1 +20 +0 C. in nitrogen for +b 5 +l <<<<
>>>>minutes and then

0844 irradiated with electron beams under the conditions shown in
0845 Table +b 1.

0846 +P The film obtained was evaluated by the following

0849 +p A sample for dielectric constant measurement was

0850 produced by forming an aluminum electrode pattern by vapor

deposition on the film obtained. This sample was examined at

0852 a frequency of $\pm 100 \pm 1$ kHz with precision LCR meter HP**b** 4284**b** 1 A,
0853 manufactured by Yokogawa-Hewlett-Packard, Ltd., by the CV
0854 method to determine the dielectric constant of the coating
0855 film.

0856 +pg,33

0857 +ps +b 2. +l Hardness

0858 +p A Barkobitch type indenter was attached to a

0859 nanohardness meter (trade name: Nanoindentator XP)

0860 manufactured by MTS, and this hardness meter was used to

0861 determine the universal hardness of the organic silica-based

0862 film formed on the silicon wafer. Hardness was measured by

0863 Mechanical Properties Microprobe method.

0864 +ps +b 3. +l Carbon Content

0865 +p The number of carbon atoms was determined by the

0866 Rutherford backward scattering method and hydrogen forward

0867 coil scattering method. The carbon content is shown in terms

0868 of the proportion of carbon atoms to all atoms (% by mole).

0869 +ps +b 4. +l Examination for Silicon Carbide Bond

0870 +p Whether or not silicon carbide bonds were present was

0871 judged by infrared spectroscopy based on the absorption around

0872 +b 890 +l cm+hu +31 1 +l attributable to the stretching vibration of <<<<

>>>>Si+13 C+13 Si.

0873 +ps +b 5. +l Cracking Resistance

0874 +p The composition sample was applied to an +b 8+1 -inch silicon

0875 wafer by spin coating in such an amount as to result in a cured

0876 coating film having a thickness of +b 1.6 +l +82 m. This coating film

0877 was dried first at +b 90+1 +20 +0 C. on a hot plate for +b 3 +l <<<<

>>>>minutes and then

0879 the coated substrate was burned for +b 60 +l minutes in a +b 420+1 <<<<

>>>>+20 +0 C. vacuum

the coated substrate was burned for +b 60 +l minutes in a +b 420+1 <<<<

0881 incised with a knife and then immersed in pure water for +b 5 +1 hours.
0882 Thereafter, the incision of the coating film was examined with
0883 a microscope to evaluate cracking resistance based on the

0884 +pg,34

0885 following criteria.

0886 +p1 +602 : No crack propagation was observed.

0887 +p1 +33 : Crack propagation was observed.

0888 +c1 EXAMPLES +b 2 +1 TO +b 7

0889 +P The coating compositions shown in Table +b 1 +1 were used

0890 in the same manner as in Example +b 1 +1 to obtain coating films

0891 respectively having the thicknesses shown in Table +b 1. +1 The

0892 coating films obtained were heated first at +b 80+1 +20 +0 C. in the air

0893 for +b 5 +1 minutes and subsequently at +b 200+1 +20 +0 C. in <<<<

>>>>nitrogen for +b 5

0894 +1 minutes and then irradiated with electron beams under the

0895 conditions shown in Table +b 1.

0896 +P The films obtained were evaluated in the same manner

0897 as in Example +b 1. +1 The results obtained are shown in Table +b 2.

0898 +c1 REFERENCE EXAMPLE +b 1

0899 +P The coating composition +b 1 +1 obtained in Production

0900 Example +b 1 +1 was applied to an +b 8+1 -inch silicon wafer by spin <<<<

>>>>coating

0901 to obtain a coating film having a thickness of +b 0.8 +1 +82 m. This

0902 coating film was heated first at +b 80+1 +20 +0 C. in the air for +b <<<<

>>>>5 +1 minutes

0903 and then at +b 200+1 +20 +0 C. in nitrogen for +b 5 +1 minutes. <<<<

>>>>Subsequently,

>>>>conducting

0906 electron beam irradiation.

0908 in Example +b 1. +l The results obtained are shown in Table +b 2.
0909 +P The time required for electron beam irradiation in each
0910 of Examples +b 1 +l to +b 7 +l was within +b 7 +l minutes.

PATENT #56571037.001

0911 +pg,35

0912 +t,0350

0913 +t,0351

0914 +c1 EXAMPLES +b 8 +l TO +b 14

0915 +P Each of the coating compositions shown in Table +b 3 +l was

0916 applied to an +b 8+l -inch silicon wafer by spin coating to obtain

0917 a coating film having a thickness of +b 0.8 +l +82 m. This coating film

0918 was heated first at +b 80+l +20 +0 C. in the air for +b 5 +l minutes and

0919 +pg,36

0920 subsequently at +b 200+1 +20 +0 C. in nitrogen for +b 5 +1 minutes <<<<
>>>>and then cured

0921 by heating at +b 400+1 +20 +0 C. for +b 30 +1 minutes to form on the <<<<
>>>>substrate

0922 an organic silica film having a dielectric constant of +b 2.8 +1 or
0923 lower.

0924 +P These organic silica films were irradiated with
0925 electron beams under the conditions shown in Table +b 3. +1 The time
0926 required for electron beam irradiation in each of Examples +b 8
0927 +1 to +b 14 +1 was within +b 7 +1 minutes.

0928 +P The films obtained were evaluated in the same manner
0929 as in Example +b 1. +1 The results obtained are shown in Table +b 4+1 .

0930 +t,0360

PATENT #56571037.001

0931 +pg,37

0932 +t,0370

0933 +P According to the invention, a film having a low

0934 dielectric constant and excellent mechanical strength can be

0935 provided.

0936 +pg, 38

0937 +cm What is claimed is:

0938 +cm 1. A process for producing a silica-based film, the process

0939 comprising irradiating a film comprising at least one siloxane <<<<
>>>>compound with electron beams

0940 at an irradiation dose of from +b 1 +1 to +b 200 +1 +82 C/cm+hu 2 +1 <<<<
>>>>to thereby convert the film into a film having a

0941 dielectric constant of +b 3 +1 or lower and having silicon carbide <<<<
>>>>bonds represented by Si+13 C+13 Si.

0942 +cm 2. The process as claimed in claim 1, wherein the

0943 silica-based film has a dielectric constant of +b 2.8 +1 or lower.

0944 +cm 3. The process as claimed in claim 1, wherein the siloxane <<<<
>>>>compound is a

0945 product of the hydrolysis and/or condensation of at least one <<<<
>>>>compound selected from the

0946 group consisting of compounds represented by the following formula <<<<
>>>>(+b 1+1):

0947 +ps

0948 +ti R+hu 1+hd a+l Si (OR+hu 2+l)+hd 4-a+tm (+b 1+l)

0949 +ps

0950 +ps wherein R+hu 1 +l represents a monovalent organic group or a <<<<
>>>>hydrogen atom; R+hu 2 +l represents a

0951 monovalent organic group; and a is an integer of +b 0 +1 to +b 2,

0952 +ps and compounds represented by the following formula (+b 2+1):

$$>>> \text{Si}(\text{OR} + \text{hu}_{5+1}) + \text{hd}_{3-c+1} \text{R} + \text{hu}_{6+\text{hd}_c+\text{tm}} (+\text{b}_{2+1})$$

0955 105

>>>>same or different and each represents a monovalent

0957 organic group; b and c may be the same or different and each is an <<<<

>>>>integer of +b 0 +1 to +b 2; +1 R+hu 7 +1

0958 represents an oxygen atom or a group represented by +13 (CH+hd 2+1 <<<<

>>>>)+hd n+1 +13 , wherein n is +b 1 +1 to +b 6; +1 and d is +b 0 +1

0959 or +b 1.

0960 +cm 4. The process as claimed in claim 1, wherein the film

0961 comprising a siloxane compound is an organic silica film.

0962 +cm 5. The process as claimed in claim 1, wherein the film

0990 to +b 200 +1 +82 C/cm+hu 2+1 .

0067 +pg,4

0068 a process for producing an insulating film which has an
0069 excellent balance between dielectric constant and mechanical
0070 strength and is suitable for use as a dielectric film in
0071 semiconductor devices and the like.

0072 +P Another object of the invention is to provide a process
0073 for producing a silica-based film which comprises irradiating
0074 a film comprising at least one siloxane compound with electron
0075 beams.

0076 +P Still another object of the invention is to provide
0077 a film obtained by the process and an insulating film.

0078 +cl DETAILED DESCRIPTION OF THE INVENTION

0079 +P In the invention, a film comprising at least one
0080 siloxane compound (hereinafter referred to as +37 coating film,+38)
0081 is formed on a substrate.

~~prepared by~~ ^{for} forming the coating film, a coating composition
>>> dissolving at least one siloxane compound in an

0083 organic solvent (hereinafter referred to as +37 coating
0084 composition+38) is applied to a substrate and the organic solvent
0085 is removed from the coating.

0086 +P Ingredient (A) which is the siloxane compound in the
0087 invention is a product of the hydrolysis and/or condensation
0088 of at least one compound selected from the group consisting
0089 of compounds represented by the following formula (+b 1+1)

0092 +ti $R+hu\ 1+hd\ a+1\ Si(OR+hu\ 2+1\)+hd\ 4-a+tm\ (+b\ 1+1\)$

0093 +ps

where R represents a hydrogen atom or a monovalent organic

0126 +pg,6

0127 fluorotriethoxysilane, fluorotri-n-propoxysilane,

0128 fluorotriisopropoxysilane, fluorotri-n-butoxysilane,

0129 fluorotri-sec-butoxysilane, fluorotri-tert-butoxysilane,

0130 and fluorotriphenoxysilane;

0131 tetraalkoxysilanes such as tetramethoxysilane,

0132 tetraethoxysilane, tetra-n-propoxysilane,

0133 tetraisopropoxysilane tetra-n-butoxysilane, tetra-sec-butoxysilane,

0134 tetra-tert-butoxysilane, and

0135 tetraphenoxysilane;

0136 alkyltrialkoxysilanes such as methyltrimethoxysilane,

0137 methyltriethoxysilane, methyltri-n-propoxysilane,

0138 methyltriisopropoxysilane, methyltri-n-butoxysilane,

0139 methyltri-sec-butoxysilane, methyltri-tert-butoxysilane,

0140 methyl triphenoxysilane, ethyl trimethoxysilane,

0141 ethyltriethoxysilane, ethyltri-n-propoxysilane,

0142 ethyltriisopropoxysilane, ethyltri-n-butoxysilane,

0143 ethyltri-sec-butoxysilane, ethyltri-tert-butoxysilane,

0144 ethyltriphenoxysilane, vinyltrimethoxysilane,

0145 vinyltriethoxysilane, vinyltri-n-propoxysilane,

0146 vinyltriisopropoxysilane, vinyltri-n-butoxysilane,

0147 vinyltri-sec-butoxysilane, vinyltri-tert-butoxysilane,

0148 vinyltriphenoxysilane, n-propyltrimethoxysilane, n¹

0149 propyltriethoxysilane, n-propyltri-n-propoxysilane, n-propyltriisopro<<<<

0151 n-propyltri-tert-butoxysilane,

0152 n-propyltriphenoxysilane, isopropyltrimethoxysilane,

isopropyltriethoxysilane, isopropyltri-n-propoxysilane,

- 0321 +pg,13
- 0322 -bis(ethoxydiphenylsilyl)propane. Preferred of these are
- 0323 hexamethoxydisilane, hexaethoxydisilane,
- 0324 hexaphenoxydisilane, +b 1,1,2,2+1 -tetramethoxy-+b 1,2+1
- 0325 -dimethyldisilane, +b 1,1,2,2+1 -tetraethoxy-+b 1,2+1 -dimethyldisilane,
- 0326 +b 1,1,2,2+1 -tetramethoxy-+b 1,2+1 -diphenyldisilane, +b 1,1,2,2+1
- 0327 -tetraethoxy-+b 1,2+1 -diphenyldisilane, +b 1,2+1 -dimethoxy-+b 1,1,2,2+1
- 0328 -tetramethyldisilane, +b 1,2+1 -diethoxy-+b 1,1,2,2+1
- 0329 -tetramethyldisilane, +b 1,2+1 -dimethoxy +b 1,1,2,2+1
- 0330 -tetraphenyldisilane, +b 1,2+1 -diethoxy-+b 1,1,2,2+1
- 0331 -tetraphenyldisilane, bis(hexamethoxysilyl)methane,
- 0332 bis(hexaethoxysilyl)methane,
- 0333 bis(dimethoxymethylsilyl)methane,
- 0334 bis(diethoxymethylsilyl)methane,
- 0335 bis(dimethoxyphenylsilyl)methane,
- 0336 bis(diethoxyphenylsilyl)methane,
- 0337 bis(methoxydimethylsilyl)methane,
- 0338 bis(ethoxydimethylsilyl)methane,
- 0339 bis(methoxydiphenylsilyl)methane, and
- 0340 bis(ethoxydiphenylsilyl)methane.
- 0341 +P In the invention, it is preferred to use a combination
- 0342 of an alkyltrialkoxysilane and a tetraalkoxysilane among the
- 0343 compounds (+b 1+1) and (+b 2+1) enumerated above. In this case, the
- 0344 proportion of the tetraalkoxysilane is generally from +b 5 +1 to +b <<<<

>>>>preferably

0346 from +b 15 +1 to +b 70+1 % by weight and that of the alkyltrialkoxysilane

0963 +pg,39

0964 comprising a siloxane compound has a thickness of from +b 0.05

0965 +l to +b 3 +l +82 m.

0966 +cm 6. The process as claimed in claim 1, wherein the electron beam

0967 irradiation is conducted at an energy of from +b 0.1 +l to +b 50 +l keV.

0968 +cm 7. The process as claimed in claim 1, wherein the

0969 electron beam irradiation is conducted at +b 25 +l to +b 500+l +20 +0 C.

0970 +cm 8. The process as claimed in claim 1, wherein the

0971 electron beam irradiation is conducted in an atmosphere having

0972 an oxygen concentration of +b 10,000 +l ppm or lower.

0973 +cm 9. The process as claimed in claim 1, wherein the

0974 electron beam irradiation is conducted in an inert gas

0975 atmosphere.

0976 +cm 10. The process as claimed in claim 1, wherein the

0977 electron beam irradiation is conducted at +b 133.3 +l Pa or lower.

0978 +cm 11. The process as claimed in claim 1, wherein the

0979 film comprising a siloxane compound is heat-cured at +b 300 +l to

0980 +b 500+l +20 +0 C. before being subjected to the electron beam <<<<

>>>>irradiation.

0981 +cm 12. A silica-based film obtained by the process as

0982 claimed in claim 1.

0983 +cm 13. The silica-based film as claimed in claim 12,

0984 which has a carbon content of from +b 5 +l to +b 17+l % by mole.

0985 +cm 14. A low-dielctric film comprising the silica-based

0988 film as claimed in claim 14.

0989 +cm 16. The process as claimed in claim 1 wherein the irradiation <<<<

PGP --> IDC REUSE MOVE SUMMARY SHEET FOR: 05657103 - 09/23/02 - 0127 Of 0263

Report Date/Time: 09/25/02 - 17:06

Created TEX FILE: 56571037.001

CWU Folder #: 02 - Contains The Following 1 Items:

T-0351

CWU Folder #: 03 - Contains The Following 3 Items:

T-0350 T-0360 T-0370

END OF REPORT FOR: 05657103 - 09/23/02

- MOVE WAS SUCCESSFUL
